

## ENHANCING THERMAL AND OPTICAL PROPERTIES OF PLA THROUGH COPOLYMER BLENDING FOR SUSTAINABLE PACKAGING SOLUTIONS

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This study investigates the incorporation of synthetic copolymers into a commercial poly(lactic acid) (PLA) matrix in order to enhance its thermal and optical properties by promoting sustainable and eco-friendly alternatives to traditional plastics. Commercial PLA and [P(HEMA-g-PCL)]<sub>3</sub> copolymers were blended in various concentrations (2.5%, 5%, and 10% w/w) by using melt blending and thermo-compression techniques. The resulting films were thermally characterized by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), and by UV-Visible spectrophotometry to evaluate their optical properties. The results indicated that the addition of copolymers decreased the glass transition temperature ( $T_g$ ) of PLA, by suggesting a plasticizing effect, while increasing the crystallinity percentage ( $X_c$ ), likely due to a nucleating effect. Despite a reduction in the onset degradation temperature ( $T_{005}$ ), the values remained above industrial processing temperatures (>170 °C). Star-like copolymers significantly enhanced the UV barrier properties and opacity of the PLA films. Particularly, 10% w/w copolymer addition showed a 4.7-fold increase in opacity and up to 3.1-fold increase in UV absorption. These improvements make PLA-copolymer composites highly suitable for applications requiring advanced barrier properties, such as food packaging. This research is particularly relevant in the field of bioproducts engineering, where innovative materials are essential for creating eco-friendly and high-performance materials.

**Keywords:** Poly(Lactic Acid) PLA 1. Copolymers 2. Thermal Properties 3. Barrier Properties

### 1 INTRODUCTION

In today's world, the searching for sustainable and environmentally friendly solutions has become a priority for industrial and social points of view. Commercial polymeric materials (extensively used across diverse sectors, ranging from packaging and medical products to industrial components and electronic devices) play a crucial role. However, the environmental impact associated with their widespread use has stimulated a growing interest in developing more eco-friendly alternatives<sup>1</sup>.

Poly(lactic acid) (PLA), as a rigid thermoplastic, shares basic properties that are relatively comparable to some traditional plastics such as PET and PS but notably different from polyethylene (PE) and polypropylene (PP). PLA stands out with exceptional characteristics including superb transparency, a glossy appearance, high rigidity (that facilitates thinner thermoforming parts), and the ability to maintain printing effects and twist retention. These unique attributes make PLA highly suitable for applications in various market segments, such as fibers, disposable cups, salad boxes, and cold food packaging<sup>2</sup>.

One of the most promising strategies for obtaining advancing sustainable and innovative polymeric materials involves the use of additives from natural or synthetic origins. These additives can significantly alter properties such as strength, elasticity, durability, and transparency of commercial polymers, by enhancing their profile<sup>3</sup>. PLA, derived from renewable resources like corn starch and sugarcane, is biodegradable and compostable, ensuring complete degradation<sup>4</sup>. Moreover, PLA shares industrial production capabilities similar to commodity polymers like polypropylene<sup>5</sup>.

Blending PLA with synthetic copolymers offers numerous advantages by allowing precise adjustment of material properties such as mechanical strength, flexibility and glass transition temperature. This versatility supports tailored applications across industries, from food packaging to additive manufacturing. Additionally, the incorporation of copolymers can enhance the processability of PLA, facilitating its efficient handling in manufacturing processes such as extrusion, injection molding, and additive manufacturing. This study aims to evaluate how the incorporation of copolymers influences the thermal, optical, and mechanical properties of a commercial PLA matrix, crucial attributes for industries including food packaging and additive manufacturing.

### 2 MATERIAL & METHODS

## Materials

Commercial PLA (Red 3D transparent) and [P(HEMA-g-PCL)]<sub>3</sub> copolymers were used as polymeric matrix and filler, respectively. For this purpose, the star-like copolymers synthesis was carried out by using a one-pot protocol combining simultaneously the RAFT and ROP mechanisms. The general procedure was based on similar research previously reported in the literature<sup>6</sup>.

## Preparation - Processing by melt blending and thermo-compression

To carry out the processing of the compounds, mixtures of PLA and [P(HEMA-g-PCL)]<sub>3</sub> copolymers as filler, with different filler concentrations were prepared (2.5%, 5%, and 10% w/w relative to the mass of PLA). This process was carried out by using a mini-mixer (Atlas Laboratory), which operated at a constant temperature of 190°C and a rotation speed of 40 rpm for 15 minutes. This blending stage is crucial to achieve a homogeneous distribution of copolymer within the PLA matrix, which is essential to ensure the final properties of the composite material. The compounds obtained were denoted as PLA-C#, where the symbol # refers to the concentration of copolymer incorporated.

Once the compounds were obtained, films were produced by using the thermo-compression technique. This stage involved subjecting the different formulations to controlled temperature and pressure conditions by using a heated hydraulic press. The films were obtained at 190°C and 180 kg cm<sup>-2</sup> of pressure for 6 minutes. The thickness of the films was determined using a high-precision digital thickness gauge (model CM-882). Measurements were taken at 10 random locations on each film to ensure the representativeness of the data obtained. Based on these measurements, the average thickness of each film and its standard deviation were calculated, providing valuable information on the repeatability of the proposed manufacturing methodology.

## Thermal characterization

Thermal properties were determined by Differential Scanning Calorimetry (DSC), by using a TA Q8000 calorimeter. Tests ( $\approx 10$  mg sample) were performed under a nitrogen atmosphere, from -50°C to 200°C, at a heating rate of 10°C min<sup>-1</sup>. The reported data was taken from the second heating cycle in order to eliminate sample's thermal history. From these thermograms, the transition temperatures of the obtained compounds and the final crystallinity percentage ( $X_c$ ) of each formulation were determined. The  $X_c$  values were calculated according to equation 1.

$$X_c (\%) = \frac{\Delta H \times w}{(\Delta H^\circ) \times 100} \quad (1)$$

where  $\Delta H$  corresponds to the fusion enthalpy of the sample,  $\Delta H^\circ$  is the fusion enthalpy for 100% crystalline PLA (93 J g<sup>-1</sup>), and  $w$  is the PLA fraction present in the compound<sup>7</sup>.

The thermal stability of the samples was determined by using a thermogravimetric balance (TGA), using a Shimadzu-50 equipment. The samples were heated from 25°C to 700°C at a heating rate of 10°C/min, using nitrogen as inert atmosphere (50 mL min<sup>-1</sup>). Mass loss curves vs temperature and the onset degradation temperature  $T_{0.05}$ , corresponding to a 5% w/w mass loss, were recorded.

## Evaluation of UV and visible radiation barrier capacity

The optical properties of PLA and PLA-C# films were evaluated from the absorption spectra in the wavelength range between 200 and 700 nm. These spectra were obtained by using a UV-Visible spectrophotometer DR6000 (Hach, USA). For this analysis, films were cut into rectangles of 10 x 30 mm and placed inside a quartz cell with an optical path of 10 mm. The absorption capacity in the UV range was calculated as the area under the curve in the spectrum region between 250 and 300 nm, while opacity was calculated in the interval between 400 to 700 nm. On the other hand, transparency was determined based on the absorbance value at 600 nm divided by the average thickness of the film. It is important to note that the optical properties were analyzed according to the ASTM D1003-00 standard, which corresponds to the standard test method for haze and luminous transmittance measurement in transparent plastics<sup>8</sup>.

## 3 RESULTS & DISCUSSION

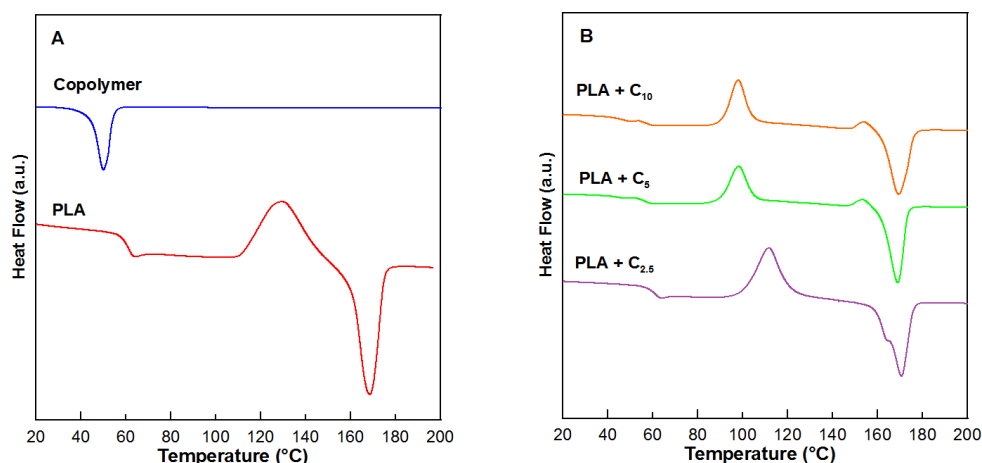
Figures 1A and 1B show the thermograms obtained by DSC for PLA matrix, [P(HEMA-g-PCL)]<sub>3</sub> copolymers, and their corresponding mixtures. For the commercial PLA matrix, the glass transition temperature ( $T_g$ ) was determined to be around 65 °C, with a broad exothermic peak at 132 °C corresponding to the formation of crystals during the cold crystallization of PLA<sup>9</sup>. In addition, melting temperature ( $T_m$ ) is observed at 168 °C. The  $X_c$  (%) value was calculated as 28.5%. Figure 1A also shows [P(HEMA-g-PCL)]<sub>3</sub> thermogram. In this sense, only the  $T_g$  of copolymer was detected at 62 °C.

On the other hand, Figure 1B shows thermograms from PLA composites. For PLA-C10, a slight decrease in  $T_g$  of -4 °C was observed, indicating that the presence of copolymers could be acted as a plasticizer of PLA chains, modifying their mobility in the glass transition region of the material<sup>10</sup>.

Table 1 summarize the thermal transitions of PLA and PLA composites. In addition, the  $X_c$  (%) values of PLA matrix and its compounds were also included. In general terms, an increase in the maximum  $X_c$  (%) was observed. This phenomenon could be associated with the nucleating effect produced by the incorporation of [P(HEMA-g-PCL)]<sub>3</sub> copolymers as filler in the semicrystalline PLA matrix.

TGA results are also presented in Table 1. The thermal degradation process began at 364°C for PLA ( $T_{0.05}$ ), whereas this value decreases for the compounds (from 339 °C to 358 °C). Nevertheless, this decrease in the  $T_{0.05}$  is still well above industrial

processing temperature (~170°C). Finally, a single thermal decomposition event at 364 °C was observed for PLA, whereas this value was 337 °C, 366 °C and 357 °C for the samples with 2.5%, 5% and 10% with copolymer as filler, respectively.



**Figure 1.** DSC curves for: A. Copolymer (blue) and PLA (red). B. Composite of PLA-C10 (orange), PLA-L5 (green) and PLA-L2.5 (purple).

**Table 1** Thermal properties of PLA and PLA-C#.

Sample	$T_g$ (°C)	$T_c$ (°C)	$T_f$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)	$T_{005}$ (°C)
PLA	65.0	132.0	168.0	26.5	28.5	364.0
PLA-C <sub>2,5</sub>	61.4	111.5	170.7	37.0	38.6	339
PLA-C <sub>5</sub>	57	98.1	169	42.1	42.7	364
PLA-C <sub>10</sub>	55.1	98.0	169.3	43.3	41.7	358

The addition of [P(HEMA-g-PCL)]<sub>3</sub> copolymers significantly improved the barrier properties to UV radiation and the opacity of PLA matrix. Particularly, the sample with 10% w/w copolymer showed an opacity value of 4.7 times higher when compared to PLA sample. Likewise, PLA and composites showed an absorption values to UV radiation in the range between 275 to 300 nm. UV barrier capacity ranged from 1.5 to 3.1 times higher in compounds when compared to PLA matrix. This blocking effect could be associated with the presence of copolymer particles that increased the ordering of PLA chains during the crystallization process. In addition, the increase in tortuosity in the PLA matrix generated by the presence of copolymer enhances barrier properties, as it was previously cited in the literature<sup>11</sup>.

## 4 CONCLUSION

By incorporating star-like [P(HEMA-g-PCL)]<sub>3</sub> copolymers into PLA matrix, thermal and optical properties of the resulting compounds were increased. [P(HEMA-g-PCL)]<sub>3</sub> copolymers act as a plasticizer, by improving flexibility and crystallinity of PLA. In addition, UV protection capabilities are also enhanced. These improvements align with the goal of developing high-performance materials that can replace traditional plastics in multiple industries.

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